quences in further elaborative chemistry of this reagent. Our work continues with this reagent and future efforts will be directed toward elucidation of the full scope of the reagent as well as the mechanistic process for the production of $[CF_3CF_2Cu]$ from $[CF_3Cu]$.

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Kinetics of the Isomerization of 1-Methylsilene to Dimethylsilylene

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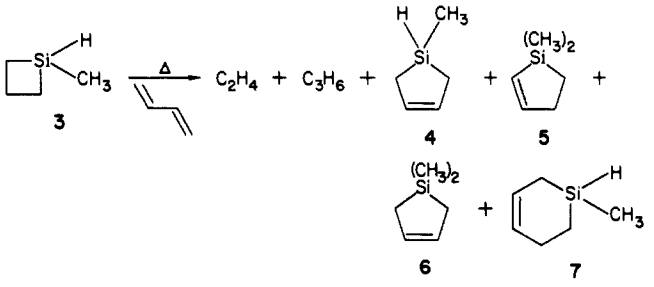
The activation barrier for the transfer of hydrogen atoms between a metal and a carbon atom is currently a subject of wide interest. In particular, the hydrogen shift that converts hydridosilenes to methylsilylenes has been the focus of numerous experimental[1-4] and theoretical studies.[5-7] The energy required for the silene isomerization has been calculated from theory[8,9] but the result is without experimental verification. We now report results of a kinetic study of the temperature dependence for butadiene trapping of 1-methylsilene (**1**) and dimethylsilylene (**2**)

$$\underset{\mathbf{1}}{H(CH_3)Si{=}CH_2} \rightarrow \underset{\mathbf{2}}{CH_3\dot{S}i{-}CH_3}$$

which allow an experimental measure of the activation enthalpy and entropy of the 1,2-hydrogen shift from a silene to a silylene.

Gas-phase pyrolysis[10] at 477.5 °C of 1-methylsilacyclobutane (**3**) (3 torr) and a 5-fold excess of butadiene in a 250-mL quartz vessel yielded ethylene and propylene in a ratio of ca. 10:1 and four different silicon-containing products: 1-methyl-1-silacyclopent-3-ene (**4**) (3%), 1,1-dimethyl-1-silacyclopent-2-ene (**5**) (4%), 1,1-dimethyl-1-silacyclopent-3-ene (**6**) (18%), and 1-methyl-1-silacyclohex-3-ene (**7**) (74%). The relevant reaction paths for



the isomerization kinetics are outlined in Scheme I.[11] Under pseudo-first-order conditions the ratio of silylene to silene adducts (six- and five-membered rings, respectively) is time invariant

Scheme I

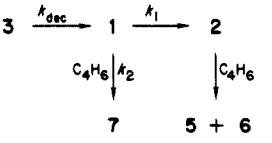


Table I. Ratio of 7/(5 + 6)

T, °C	453.3	460.2	470.6	477.5[a]	485.4
7/(5 + 6)	5.55	4.01	3.70	3.32	2.79

[a] If this value is omitted, the correlation coefficient $R = 0.999$.

Table II. Rate Constants for Decomposition of 3

T, °C	453.3	460.2	470.6	477.5	485.4
$K_{overall}$, 10^3 s^{-1}	1.09	1.69	2.86	4.29	6.19

beween 200–400 s. The equation that relates the influence of temperature to the concentration of silene and silylene products is given below:[12]

$$7/(5 + 6) = A(2)[\text{butadiene}]/A(1)e^{-(E(1) - E(2))/RT} \quad (1)$$

Product ratios, 7/(5 + 6), from the pyrolysis of **3** and butadiene at five different temperatures from 453.3 to 485.4 °C are listed in Table I. A least-squares plot of eq 1 against $1/T$ provides the slope, $E(1) - E(2) = 23.4 \pm 0.7$ kcal mol^{-1}, and the intercept, $\ln A(1)[\text{butadiene}]/A(2) = -14.5 \pm 0.5$. With the assumption that the activation energy $E(2)$ is ca. 7 kcal mol^{-1} and the preexponential $A(2) = 10^7$ dm^3 mol^{-1} s^{-1} for the cycloaddition of methylsilene to butadiene,[14] the Arrhenius parameters would be $E(1) = 30.4 \pm 0.7$ kcal mol^{-1} ($\Delta H^{\ddagger} = 28.9 \pm 0.7$ kcal mol^{-1}) and $A(1) = 9.6 \pm 0.2$ s^{-1} ($\Delta S^{\ddagger} = -18.5 \pm 0.9$ cal/(mol deg)).[15]

The preexponential term for the silene to silylene isomerization is surprisingly lower than previous experimental estimates[4,7] thus suggesting an unusually "tight" transition state for the H-shift. This observation, however, is consistent with the theoretical prediction that rotation about the Si=C bond of the silene involves pyramidalization of the hydrogens on the trigonal Si.[7] The large decrease in entropy during the hydrogen shift from Si to C may be attributed to the geometry of the vibrationally excited silene or possibly to the participation of the triplet state of the silene.[16] The lack of other data for the entropic demands of 1,2-H shifts leaves the interpretation open.

In theoretical studies, $\Delta G^{\ddagger}$ of the isomerization has been calculated to be 40.6 kcal mol^{-1} for $H_2Si{=}CH_2$[8] and 42.2 kcal mol^{-1} for $H(Me)Si{=}CH_2$.[9] The experimental measure of $\Delta G^{\ddagger}$, 42.5 kcal mol^{-1} at 470.6 °C, is in excellent but probably fortuitous agreement since it is based on an experimental *estimate* of kinetic parameters for a silene cycloaddition to butadiene.[14]

Despite the limited temperature range required by the thermal instability of the methylsilene adduct **7**, excellent first-order behavior is found for the decomposition of **3**. Rate constants over the same temperatures as above (Table II) provide the activation parameters: $A = 10^{14.9 \pm 0.3}$ s^{-1} and $E(3) = 59.1 \pm 0.1$ kcal mol^{-1}. Previously, an approximate measure of the Arrhenius plot for the decomposition of **3** has been reported[17] as $A = 10^{14.0}$ s^{-1} and $E(3)$

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= 52.6 kcal mol^{-1}, in fair agreement with this work. Finally, the similarity of the kinetic parameters reported here to those for the decomposition of other four-membered rings,[18] the thermal stability of **7** under these conditions, and the kinetics of the silene isomerization mitigate against the suggestion of a multistep diradical mechanism for the formation of **2** from **3**.

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Registry No. 1, 38062-40-0; **2**, 6376-86-9; **3**, 765-33-3; **4**, 55544-25-7; **5**, 18187-50-3; **6**, 16054-12-9; **7**, 89530-22-3; C_2H_4, 74-85-1; C_3H_6, 115-07-1; butadiene, 106-99-0.

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Spectroscopic Studies on Ferrous Non-Heme Iron Active Sites: Variable-Temperature MCD Probe of Ground- and Excited-State Splittings in Iron Superoxide Dismutase and Lipoxygenase

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The ferrous non-heme iron active sites in iron superoxide dismutase (FeSD) and soybean lipoxygenase (SBL) catalyze, respectively, superoxide dismutation[1] and lipid hydroperoxidation.[2] Structures are lacking for the ferrous sites in these proteins, and while the ferric active sites have been characterized by optical and EPR spectroscopy,[3,4] comparable results are lacking for the ferrous sites. MCD spectroscopy is a powerful probe of these systems in that selection rules allow the observation of weak d-d transitions, and the temperature dependence probes ground-state splittings.[5] Using low-temperature MCD spectroscopy we have observed significant differences in both ground and excited states of the iron sites in FeSD and SBL which relate to differences in coordination number and geometry.

FeSD and SBL were purified to homogeneity (SDS-PAGE) from *E. coli* cell paste[3] and soybeans[6] according to published procedures. The low-temperature (1.8 K), high-field (6 T) MCD spectrometer will be described elsewhere.[7]

A distinction between FeSD and SBL iron sites is evident in the excited-state spectra shown in Figure 1: near-IR optical absorption, CD, and low-temperature MCD spectra for FeSD (Figure 1A) show a single broad transition above 10000 cm^{-1} with a low extinction coefficient (ϵ = 5 M^{-1} cm^{-1}) characteristic of ligand field transitions; a second band is observed in absorption near 5000 cm^{-1}. In contrast, the near-IR CD and MCD for SBL (Figure 1B) resolve two broad bands near 10000 cm^{-1} split by approximately 1500 cm^{-1}.

The temperature-dependent MCD of these ligand-field transitions probes the iron ground states in these two enzymes. Systematic variations of temperature and field strength lead to changes in MCD intensity which may be plotted as saturation magnetization curves,[8,9] shown in the Figure 2A for the FeSD

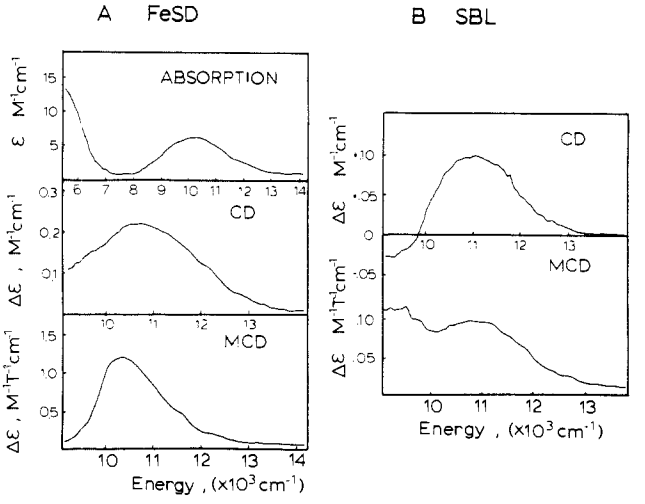

Figure 1. Excited-state spectra for non-heme iron active sites of FeSD and SBL. (A) Optical absorption, CD, and low-temperature MCD spectra for Fe^{2+} SD prepared by dithionite reduction of native enzyme in 50 mM K_2HPO_4 buffer pH 7.4. Note abscissa scale change for optical absorption spectrum. For optical absorption measurements, FeSD was lyophilized and dissolved in D_2O; the MCD sample was prepared as a glass in 50% glycerol. Samples were 3-7 mM Fe; MCD spectrum recorded at 4.2 K in a 3-mm path length cell. (B) CD and MCD spectra for native ferrous SBL in 50 mM sodium borate pH 9.0; the MCD sample was prepared as a glass in 50% glycerol. Samples were 1-2 mM Fe; MCD spectrum recorded at 4.2 K in a 3-mm path length cell. Efforts to observe these bands in absorption are complicated by turbidity at high protein concentration; we can only place an upper limit on ϵ of 5 M^{-1} cm^{-1}.

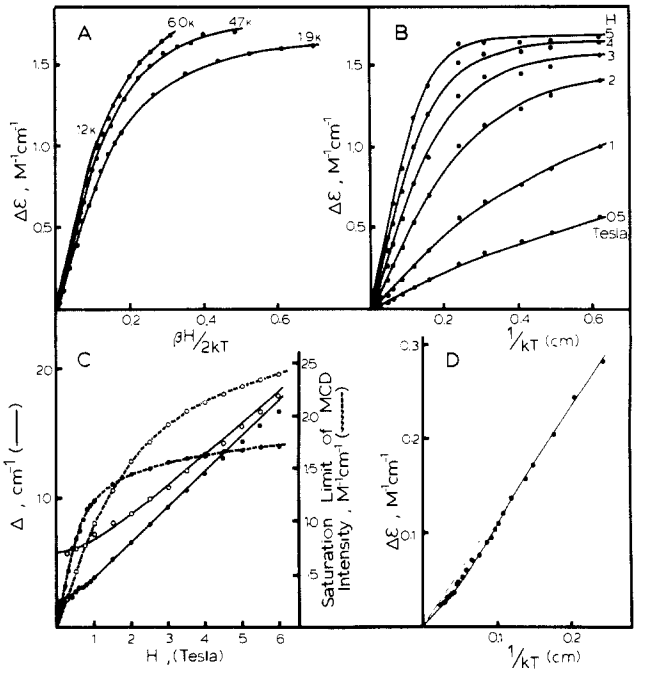

Figure 2. Temperature and field dependence of MCD intensity. (A) Saturation magnetization curves for Fe^{2+} SD for MCD intensity at 10360 cm^{-1}. Similar results are observed for SBL. (B) Replot of data in (A) as temperature dependence at constant field. (C) Splitting Δ (—) and intensity (---) for the ground $M_s = \pm 2$ doublet extracted from the curves of (B), (●) FeSD. Also shown for SBL (○).

data. Magnetic saturation occurs within a paramagnetic ground state when thermally accessible levels are depopulated from either high-field splitting or low temperature. For zero-field split systems and in particular the non-Kramers (even electron) systems in-

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